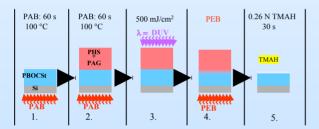


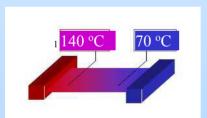
## Combinatorial Methods Study of Confinement Effects on the Reaction Front in Ultrathin Chemically Amplified Photoresists

Sub-100 nm lithography requires a better understanding of photoresist material properties and processing conditions to achieve necessary critical dimension (CD) control of patterned structures, as well as minimal line-edge roughness (LER). Besides material properties, many processing factors can impact both CD and LER, including film thickness, exposure dose, postexposure bake (PEB) temperature, PEB time, developer concentration, and development time. For example, film thickness has a significant effect on acid reaction-diffusion rate, possibly due to a change in the local chain dynamics in thin films. However, it is not completely understood how these variables contribute to CD and LER. In addition, due to the large number of parameters, development and optimization of resist systems or formulations is time consuming. Accordingly, integration of high throughput combinatorial research and development strategies provides a means to effectively conduct fundamental lithographic materials research. In this work, we adopt high throughput methods to study *PEB temperature* and *protected layer thickness* effects via a model bilayer system by using temperature and thickness gradients, respectively.

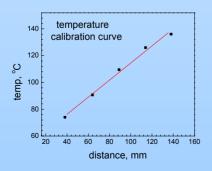
## **Bilayer Model System**

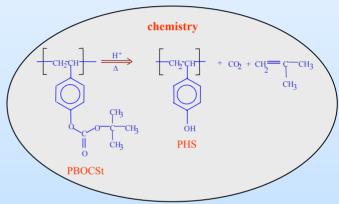


Approach 1: PEB on a contact hot plate with a temperature gradient ranging from 70 to 140 °C.

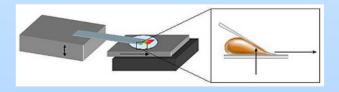


A custom built temperature gradient stage is constructed with a heated rod in one end and water-cooling in the other to provide a temperature gradient. This allows the sample to be baked at a variety of temperatures simultaneously.





**Approach 2:** flow coating to prepare a thickness gradient on bottom layer.



The solution flow coater is a custom built piece of equipment that creates thin films of polymer that have a gradient in thickness across the sample. The system works by suspending a blade edge over a substrate mounted on a computer controlled motion stage. A small bead of PBOCSt solution is inserted between the blade and the substrate. Subsequently, the stage is moved at constant acceleration to spread the solution. As the solvent evaporates a thickness gradient was formed along the direction of stage motion. Here, the solvent evaporation rate was adjusted such that the solution spread well without dewetting. To achieve this, the silicon wafer was heated to 105 °C during the flow coating process, and toluene was added to PGMEA solution.







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Fig 1. shows the post development PBOCSt layer thickness and roughness as a function of the PEB temperature. Note here that all data were collected from the same wafer, which underwent identical procedures except the baking temperature. In addition, the data points collected in the direction vertical to the temperature gradient underwent identical processing conditions enabling significant decrease of the statistical error. Accordingly, considering the complex processing and environmental sensitivity of these photoresist systems, this high throughput approach offers a promising method, which provides rapid and more complete results compared to traditional techniques.

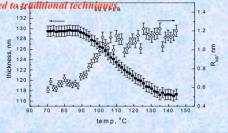
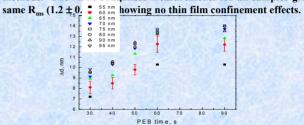


Fig 3. Shows thickness change of PBOCSt layer as a function of PEB times for different film thickness. The almost equivalent  $\Delta d$  after 60 s and 90 s PEB times indicates that the deprotection reaction has stopped after 60 s in current processing conditions. This may be due to acid trapping or neutralization via base molecules from environment contamination. Nevertheless, because the process conditions are identical within a thickness gradient specimen, the thickness dependence of  $\Delta d$  shows very similar behavior for different PEB times. Indeed, this "processing consistency" is an extra advantage of using these combinatorial methods. The AFM roughness measurements for all samples gives same  $R_{ms}$  (1.2  $\pm 0.2$   $\pm 0.0$  m howing no thin film confinement effects.



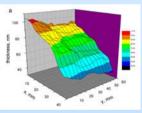


Fig 2a shows the flow coating thin film had a thickness gradient along x direction with some variations in y direction. These defects may change the interface and consequently make the reaction-diffusion rates different from a smooth surface. We use a small step (2 mm) to map the film thickness, which masks the areas with sharp peaks and valleys.

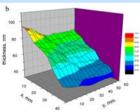


Fig 2b is a 2D plot of remaining PBOCSt thickness after PEB at  $100~^{\circ}\text{C}$  for 60~s. The change of thickness is apparent.

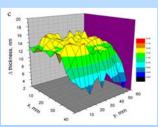


Fig 2c is the results by subtracting Fig 2b from Fig 2a. The plateau, where the original thickness is above 60 nm shows no thickness dependence. The fact that the Δd decreases with decreasing original thickness of PBOCSt layer suggests that the thin film confinement has dramatically slowed down the reaction-diffusion rate.

## **Summary**

PEB temperature can change the acid reactiondiffusion rate significantly and have effects on surface roughness and thus LER by using a PEB temperature gradient approach.

A strong thickness dependence of reaction diffusion front was confirmed by using a thickness gradient technique. The surface roughness and thus LER is independent on the thickness.

An effort to combine the PEB temperature and thickness dependencies in a single specimen is currently under way. The main challenge here is to create smooth thickness gradient.

We are developing means to fabricate exposure dose gradients and developer concentration gradients, which can be combined with PEB and thickness gradients for more extensive and efficient combinatorial studies of photoresist systems.

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